

An overview of the advanced nanomaterials science

L. Schiavo^a, A. Cammarano^b, G. Carotenuto^{a,*}, A. Longo^a, M. Palomba^a, L. Nicolais^c

^a Institute for Polymers, Composites and Biomaterials (IPCB-CNR), National Research Council, Piazzale E. Fermi 1, 80055 Portici NA, Italy

^b Materias s.r.l., Corso Nicolangelo Protopisani, 50 - 80146 Naples, Italy

^c Engineering Faculty, University of Naples "Federico II", Corso Nicolangelo Protopisani, 50 - 80146 Naples, Italy

ARTICLE INFO

Dedicated to Professor Howard Alper, in recognition of his outstanding contributions to organic chemistry and catalysis, and his tireless work to shape and strengthen science policy.

Keywords:

Nanomaterials
Nanotechnology
Nano-sizing
Terminology
2-D gold
Metallic aerogels

ABSTRACT

Modern technological solutions require more and more adequate material characteristics for their optimal operation; some of these requirements are: (i) fine control over the material properties, (ii) multiple properties combination (multi-functionality), and (iii) availability of new physical, chemical, mechanical, thermal, etc. characteristics. Most of such needs can be successfully achieved by nano-structuring the ordinary inorganic/organic solid matter. Owing to surface effects, electron confinement, changes in the solid-state band structure, and many other size-dependent physical phenomena, nanoscopic matter behaves much differently from traditional massive materials. The success of nano-structuring is just related to the opportunity to diversify the characteristics of solids that such an approach offers to the traditional material science fields. Therefore, ceramics, metals, semiconductors, polymeric/organic materials can widely benefit of the extraordinary opportunities and potentialities of the nanoscaling methods. Here, the basic aspects of nanomaterials have been synthetically described in order to prove the efficacy of this approach and the variety of potentialities and opportunities offered to scientists working in this fascinating field of knowledge. In particular, it has been presented in some details the following advanced nanocrystalline structures: metallic aerogels of silver and palladium, graphite nanoplatelets aerogel, single-crystal gold quantum-wells, natural clinoptilolite lamellas, polymer-supported graphene, micronic silver nanowires, sub-micronic cobalt nanoparticles, graphite oxide; and the following semi-cristalline: gold, silver, palladium and iron nanoparticles embedded in an amorphous polymer.

1. Introduction

In the last decade, nanoscience has represented a great revolution in materials science and it still constitutes an absolutely new and widely used approach [1,2]. However, pioneering works on nanomaterials look back to 1904, when Richard Adolf Zsigmondy (Nobel Prize in Chemistry, 1925) has developed nanocomposites of colloidal gold and gelatine that reversibly changed the color from blue to red upon swelling with water [3]. In order to explain the mechanism of nanocomposite color change, he suggested that the material optical absorption must be also influenced by the inter-particle distance. The success of this special area of materials science comes from the unique possibility offered by the nanoscience to multiply the properties that can be obtained by the solid matter [4]. Complexity is one of the prerogatives of modern materials and the nano-structuring of solid matter constitutes a valid way towards it [5,6]. Complexity in material science means capability to satisfy multiple technological requirements, possibility to optimize all final material properties and ability to reach characteristics that are not

ordinarily present in the already available materials. There are many new trends in the area of modern materials research, however nano-sizing of both hard and soft matter still represents a rapidly growing activity field, where new important results are continuously achieved. Size scaling allows new properties to arise since matter falls in some 'anomalous conditions', where surface matter prevails on bulk matter, electrons move in spatial regions whose extension is comparable with their wavelength, matter transforms from continuous to molecular type, etc. These novel properties could be technologically useful and in addition properties in nanomaterials are frequently combined in a very unusual manner. It is typically observed for example their combination with perfect optical transparency, which leads to magnetic-optically transparent materials, fluorescent-optically transparent materials, coloured-optically transparent materials, etc.

Now, it must be considered the reason for which nanostructured materials and nanotechnology are so much important for the progress of the modern society. The progress of the current technologies is strictly related to the availability of new materials. In particular, the strong

* Corresponding author.

E-mail address: giancaro@unina.it (G. Carotenuto).

<https://doi.org/10.1016/j.ica.2023.121802>

Received 29 June 2023; Received in revised form 5 October 2023; Accepted 5 October 2023

Available online 7 October 2023

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technological need for materials with widely diversified property combination has required the development of more and more diversified varieties of material classes. Diversification approaches have been based on the chemical synthesis, like for example the polymerization, which involves the sequential combination of different types of monomers, thus leading to different types of linear polymeric materials (thermoplastics) or three-dimensional networks (thermosetting resins). The preparation of composites (ceramic-metal, metal-polymers, ceramic-polymers, etc.), where different solid-phases are combined together, has represented a further possibility of diversification just like semiconductor doping and other procedures useful to multiply/control the solid material properties. Both homogeneous and heterogeneous polymeric blends and other types of hybrid solids have represented for years the possible ways for multiplying the properties of the available plastics. In the past as in the last times also the use of natural substances (eventually chemically modified) has represented a solution to the problem of making possible many properties combination. Owing to the strict correlation between morphology and property, the matter nanoscaling tool plays a fundamental role in the context of diversify the physical, chemical, mechanical, thermal, etc. properties of matter and to control them.

Here, the most relevant aspects of the nanoscale world are shortly presented in order to underline to scholars the great technological potentiality of this more and more valid material science tool. In particular, some examples of nanomaterials developed by our research group in the last decay have been described in few details in order to show our contribution to this important research field.

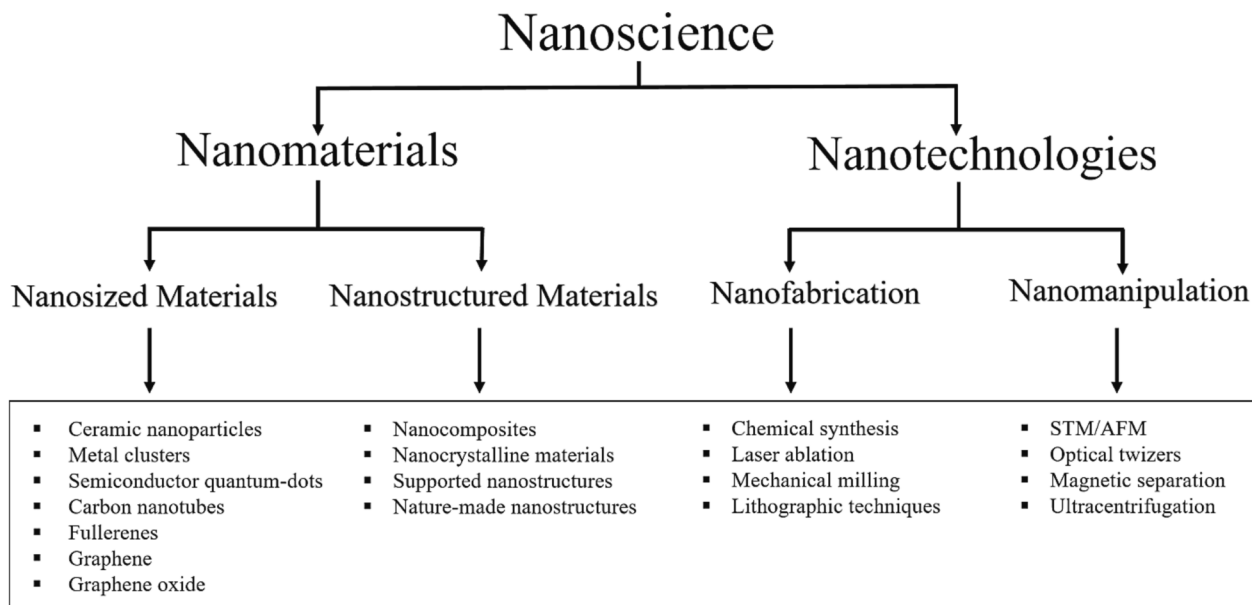
2. Nano-sized materials

Nanoscience involves two different knowledge areas: nanomaterials and nanotechnologies (see Scheme 1). The nanomaterials area concerns the investigation of structure, properties and technological applications of both the nano-sized and the nano-structured material classes; while nanotechnologies principally deals with nanomaterial preparation.

Nano-sized materials mainly consist of: ultra-fine powders of different chemical natures (i.e., ceramic, metallic, organic/polymeric, and semiconductor nanophases) and shapes (e.g., spherical/polyhedral, planar, linear and more complex regular shapes); carbon nanotubes (MW-CNTs and SW-CNTs) [7]; fullerenes (e.g., C₆₀, C₇₀) [8]; graphene oxide, graphene and other carbonious nanostructures [9,10];

semiconductor quantum-dots (e.g., mainly chalcogenides like CdS, ZnS, PbTe) [11]; polyoxometalate-based framework [12–25], etc. However, the nanoworld includes a very large variety of quite uncommon and unusually shaped nano-objects that are continuously disclosed and deeply investigated in their anomalous physical/catalytic properties, like nano-stars [26], nano-cubes, nano-scrolls, etc.

Owing to the strict dependence of properties on morphology, nano-sized materials are categorized according to the number of their finite dimensions [27]. For example, the graphene nanoplatelets (few-layer graphene) are defined as two-dimensional (2-D) nanostructures because these elements have very negligible heights (a few nanometers) (see Fig. 1a). This type of nanomaterial is more generally named quantum-well, since quantum-confinement is involved only in one dimension. As visible in Fig. 1b and c, elemental gold also forms 2-D lamellar crystals on a nanoscopic scale because this type of shape corresponds to the gold single-crystal texture. In particular, these very large and regularly-shaped 2D-gold nanoplatelets have been generated inside a polymeric matrix (e.g., thermoplastics) by using a technique based on the Oswald ripening mechanism. The Oswald ripening, a phenomenon that was discovered by Wilhelm Ostwald in 1896, is a thermodynamic process that usually takes place in colloidal suspensions, but it can happen also in multiphase liquid systems like dispersions of metal in molten polymers (i.e., polymer-embedded metal particles like the gold-polymer nanocomposites) at sufficiently high temperatures and it involves a slow but progressive change of the inhomogeneous structure (i.e., polyshaped or polydispersed solid phase) over the time by small crystals dissolution/re-precipitation onto larger crystals. This phenomenon can be advantageously exploited to obtain a polymeric dispersion of large regularly-shaped 2D-gold nanoplatelets, as shown in Fig. 1b,c. Indeed, in gold nanoparticles-polymer systems, small gold particles dissolve in the polymer and redeposit on the surface of the larger crystals that grow in size and also improve the regularity of their shape by recrystallization. In this case, gold nanoparticles have been generated in poly(methyl methacrylate) (PMMA) and amorphous polystyrene (PS) matrices by decomposition of AuCl molecules (i.e., gold(I) chloride molecules), which is a covalent inorganic salt quite soluble in non-polar organic matrices. The obtained AuCl-PMMA and AuCl-PS solid solutions have been heated at ca. 300 °C to produce a polymer-embedded nano-sized gold solid phase; successively these systems have been thermally annealed at a constant temperature (150 °C) for a few hours, in order to allow the Oswald ripening process to take place and transform the



Scheme 1. The nanoscience framework.

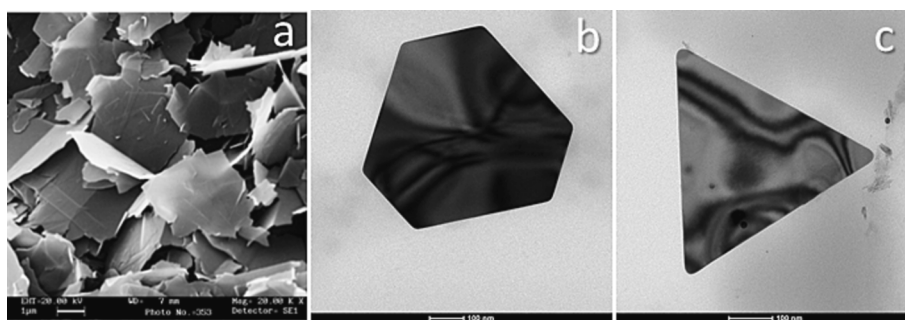


Fig. 1. Examples of 2-D nanostructures: graphite nanoplatelets (a) and gold nanocrystals in PMMA (b,c).

dispersion of shapeless crystals in few large and regularly-shaped 2D-gold nanoplatelets.

Similarly, nano-rods, nano-wires, and nano-tubes (e.g., single-wall and multi-wall carbon nano-tubes) are one-dimensional (1-D) nanostructures since they have only one finite size and the other two dimensions are negligible. Fig. 2a,b show a typical carbon nanotube bundle (Aldrich product) and silver nanowires. In particular, silver dodecyl-thiolate ($\text{AgC}_{12}\text{H}_{25}$) is a solforganic salt that produces pure

elemental silver by thermal decomposition at ca. 200 °C (dodecyl-disulphide, a waxy substance, is generated as by-product). Owing to the low solubility of these metal thiolates in alcohol (e.g., ethanol), this metallic silver precursor can be synthesized by a precipitation reaction, that takes place when an alcoholic solution of the inorganic salt (silver nitrate, AgNO_3) is mixed with a dodecyl-thiol solution in ethanol. These nanowires result because of the particular tubular crystalline structure of the normal-alkyl thiolate precursor.

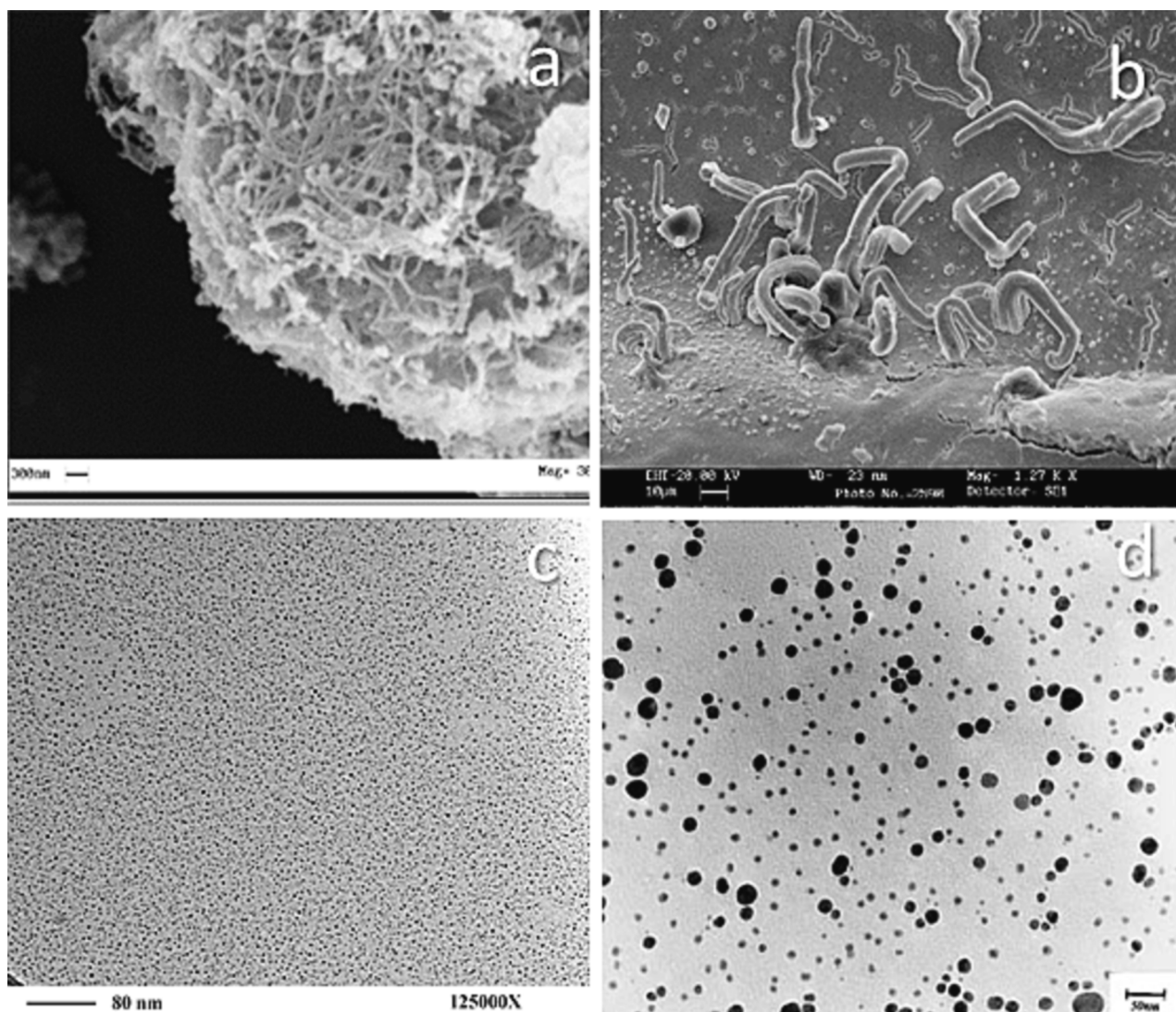


Fig. 2. Examples of 1-D (a,b) and 0-D (c,d) nanostructures. Multi-wall carbon nanotubes (MW-CNTs) bundle (Aldrich) (a), silver nanowires (b), silver atomic clusters embedded in an amorphous polystyrene matrix (c) and poly(vinyl pyrrolidone) (PVP) matrix (d).

Yet, nanoscopic spherical particles are categorized as zero-dimensional (0-D) nanostructures because they have three negligible dimensions, see Fig. 2c,d, and, depending on their size, they can fall in the quantum-dots class, like the atomic metal clusters (polyhedrals with a diameter of a few nanometers) or in the nanoparticles class (diameter of a few nanometer tens). The polymer-embedded silver metal clusters shown in Fig. 2c have been obtained by an *in situ* synthesis technique, based on the thermal decomposition of a metallic silver precursor dissolved in the polymer. Alkane-thiolates are chemical compounds very useful as precursor for the preparation of metallic nanostructures, indeed owing to the low electronegativity of the sulphur atom, these organosulfur salts have a nonpolar nature (the metal-sulphur bond is an heteropolar covalent bond). As a consequence, the metallic thiolates dissolve in nonpolar media like the molten linear polymers, thus producing very homogeneous systems (i.e., polymer solutions of metal thiolates). In addition, such chemical compounds are thermally unstable and noble-metal thiolates decompose at very convenient temperature values, fully compatible with the thermal stability of most polymers, leading to the pure metallic phase and an organic disulphide (RSSR) as by-product. In particular, the thermolysis of most metal thiolates takes place at temperatures ranging between 100 and 200 °C. Differently, thiolates of transition metals lead to the formation of chalcogenides (precisely, metal sulphides, like CdS, ZnS, CuS, etc.) and an organic sulphide (RSR). The metallic phase precipitates in the viscous polymeric matrix, thus generating metallic clusters or nanoparticles, depending on the precursor concentration (dilute thiolate solutions in polymer generate very small metal cluster dispersions).

In the preparation of the silver nanoparticles embedded in polyvinylpyrrolidone (PVP) shown in Fig. 2d, elemental silver was produced by chemical reduction of the ionic precursor (Ag^+) by alcohol. In particular, a PVP solution in ethylene glycol was mixed with a concentrated silver nitrate solution in ethylene glycol under stirring at room temperature. After the formation of silver nanoparticles (the system becomes yellow because of the surface plasmon resonance of nanoscopic silver), the colloidal suspension was mixed with a large amount of pure acetone in order to precipitate the Ag/PVP nanocomposite.

The nanoscopic sizes in all previously cited nanomaterial classes (i.e., lengths lower than 100 nm or, as required for some phenomena like the electron confinement, lower than 10 nm) are needed to allow the anomalous properties of mesoscopic solids to disclose.

Nano-sized materials can be used lonely (for example, as MR contrast agents and other markers in medicine, surface-enhance Raman scattering sensors, drug-delivery devices, etc.) but also in a supported form with substrates like Si wafer, SiO_2 plates, polymeric films, paper, textiles, etc. or in an embedded form (nanocomposites) to generate massive materials (bulk materials) that can be handled and used for the practical technological applications. Polymer-embedded nanoparticles [28–30] (see Fig. 2c,d) are a classical technological solution used to exploit the unique physical properties of nanoscopic metal and semiconductor solids by functionalizing polymeric matrices with ‘neutral’ properties, like the optical plastics (i.e., amorphous polymers, perfectly transparent and colourless and with a refractive index close to that of glass; typical optical plastics are PMMA, PS, PC).

As visible in Fig. 3a, these optical-grade nanocomposites look like homogeneous solid phases (i.e., solid solutions); however they are heterogeneous materials, or more precisely ‘nano-heterogeneous’ materials, since their heterogeneity can be disclosed only on a nanometric scale [31], for example by using microscopy techniques (e.g., transmission electron microscopy, TEM) or the Tyndall effect checking (see Fig. 3b).

The possibility to access new physical/chemical properties by reducing the ordinary solid matter to a nanometric scale is related to several physical phenomena like for example: (i) the capability of making surface matter prevailing over bulk matter; (ii) the quantum-confinement (i.e., electron confinement in potential wells, wires or dots); (iii) the transformation of continuous electronic band structure in

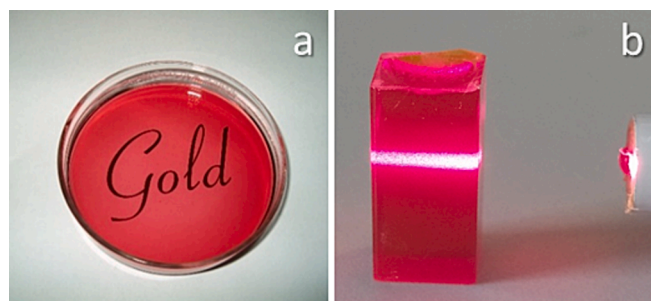


Fig. 3. Apparent homogeneity of Au-PVP nanocomposites (a) and method based on the Tyndall effect used for checking the nano-heterogeneity of epoxy-embedded Au nanoparticles (b).

discrete levels (similar to the molecular electronic structure of aromatic compounds); (iv) the change of the predominant surface atoms type (that is, edge and corner atoms despite the basal-plane atoms), etc. However, the above cited cases are only a few examples of the various possibilities that may result from scaling the solid matter to a nanoscopic size. The effect of particle size reduction on the material properties can be readily understood from the following consideration on the total energy content of a solid [32]. The total energy of a solid phase, E_{tot} , consists of two contributions, the internal energy, E_i , and the surface energy, E_s :

$$E_{tot} = E_i + E_s = e_i \cdot V + \gamma A \quad (1)$$

where e_i is the internal energy per unit volume and γ is the interfacial energy per unit surface area, while V and A are the total volume and surface area of the considered matter form, respectively. The contribution of the two terms are not always equal; indeed, depending on the conditions, one or the other term may prevail. It can be easily seen as the dominance of these contributions depends only on a geometric factor. In fact, the above equation, expressed per unit volume, reads:

$$(E_{tot})_v = e_i + \gamma(A/V) \quad (2)$$

Since e_i and γ are intrinsic properties of that specific chemical substance, the only variable quantity is A/V . If this ratio is large (e.g., $A/V \sim 10^4\text{--}10^7 \text{ cm}^{-1}$ for particles of 1–100 nm), the second term becomes significant. The properties of matter are greatly affected by the surface energy contribution to the total energy of the system. It is obvious that the large value of A/V can be achieved by having one, two, or three dimensions rather small, resulting in 2-D, 1-D, and 0-D nano-sized materials.

Interestingly, these anomalous properties of nanosized solids can be continuously and indefinitely tuned by adding/removing single atoms or molecules to/from the nanoparticle. As shown in Fig. 4, even

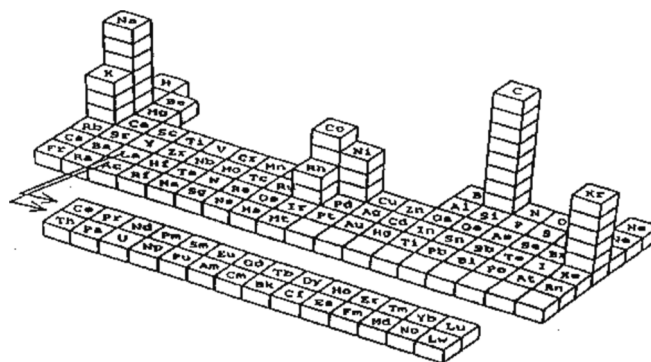


Fig. 4. 3D periodic table of elements. The vertical development, that is given for some elements as an example, represents the dependence of nanostructure properties on size/nuclearity of the solid phase.

elemental substances on a nanometric scale can have size-dependent physical/chemical properties (e.g., super-paramagnetism, surface plasmon resonance, super-catalytic effect).

In addition, surface plasmon resonance (SPR), which corresponds to the metal particle capability to absorb light because of its easy polarizability, in alloyed bimetallic particles like $\text{Ag}_x\text{Pd}_{1-x}$ can be widely tuned by changing the alloy composition. Indeed, the maximum absorption wavelength, $\lambda_{a,\max}$, approximately changes according to the following simple mixture law [33]:

$$\frac{1}{\lambda_{a,\max}^2} = \frac{x}{\lambda_{\text{Ag},\max}^2} + \frac{1-x}{\lambda_{\text{Pd},\max}^2} \quad (3)$$

where, x is the volume fraction of component one and $\lambda_{\text{Ag},\max}$, $\lambda_{\text{Pd},\max}$ are the wavelengths of maximum SPR absorption intensity of the two pure metals. Light-stable optical limiters (e.g., UV-shields, colour filters) can be fabricated by combining optical plastics (e.g., PC, PS, PMMA, epoxy) with alloyed bimetallic nanoparticles (e.g., Au/Ag, Ag/Pd).

Also the emission frequency of fluorescent semiconductor quantumdots can be widely modified by changing their size, because the band-gap energy value is strictly size-dependent.

3. Nano-structured materials

Nanostructured materials correspond to those macroscopic materials whose texture is made of tinny (nanoscopic) features [34,35]. Globular, rod-like and plate-like nano-elements can constitute the building blocks of nanostructured materials. Even natural substances could belong to this nanomaterial class. For example, the mineral substance named clinoptilolite (a very common type of natural zeolite) is made of 40 nm thick lamellar crystals stacked together in a very compact way (see Fig. 5), because of the extremely high pressure that has act on this geomorphic solid substance for millions of years. Graphite is a further typical example of naturally-occurring nanostructured material since it is made of 3.45 Å thick sheets of carbon atoms close-packed together. Nano-crystalline metals prepared by mechanical alloying is another recently developed class of nanostructured solids with anomalous properties that have received wide attention in the material science community because of their anomalous mechanical and physical properties (e.g., high electrical resistivity, low thermal conductivity, high thermal expansion coefficient).

A further important class of artificial nanostructured materials is represented by the aerogels [36,37]. Ceramic and graphene aerogels are the most famous types. Silica aerogel was the first aerogel type that has been developed. It is characterized by exceptional thermal insulating characteristics and very low density [36]. Differently, graphene aerogels combine very good electrical and thermal conductivity characteristics to

a high surface development [38–40]. Also metals have been produced in form of aerogels but they are little known [41,42]. Polymer-embedded noble metal nanoparticles constitutes the typical precursors used for preparing these metallic aerogels [43]. Such precursors can be easily obtained from metallic colloids by the co-precipitation technique, which consists in the addition of a non-solvent to the colloidal suspension [44]. In particular, the metal colloid is obtained by reducing a noble metal salt by alcohol in presence of poly(vinyl pyrrolidone) (PVP), as steric surface stabilizing agent. Since acetone is mixable with alcohols but PVP is insoluble in acetone, the addition of a large amount of acetone to the metal colloid causes the prompt precipitation of a solid phase (PVP-embedded nanoparticles). For example, in the preparation of Pd aerogels, nanoparticles of palladium embedded in PVP have been obtained by reducing a palladium salt (K_2PdCl_4) with ethylene glycol in presence of PVP, and then adding acetone to the obtained colloidal suspension (see Fig. 6a) [44]. Then, the polymeric matrix is completely burned in air at ca. 400 °C, leaving the contained noble metal nanoparticles organized in form of aerogel (see Fig. 6b) [43]. Indeed, owing to the high surface free-energy content of palladium nanoparticles, they promptly

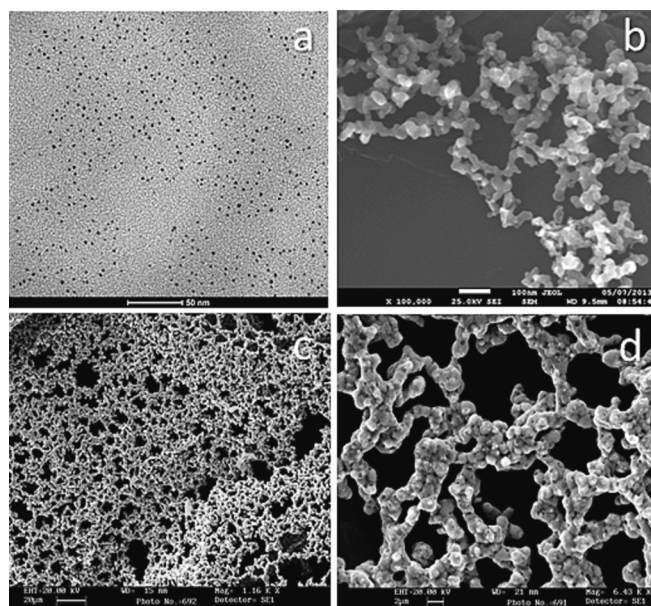


Fig. 6. Pd aerogel precursor consisting in PVP-embedded Pd nanoparticles obtained by Pd(II) reduction with ethylene glycol in presence of PVP (at 90 °C for 2 h) (a); SEM-micrograph of the obtained Pd aerogel (b); SEM-micrograph of the silver aerogel (c,d).

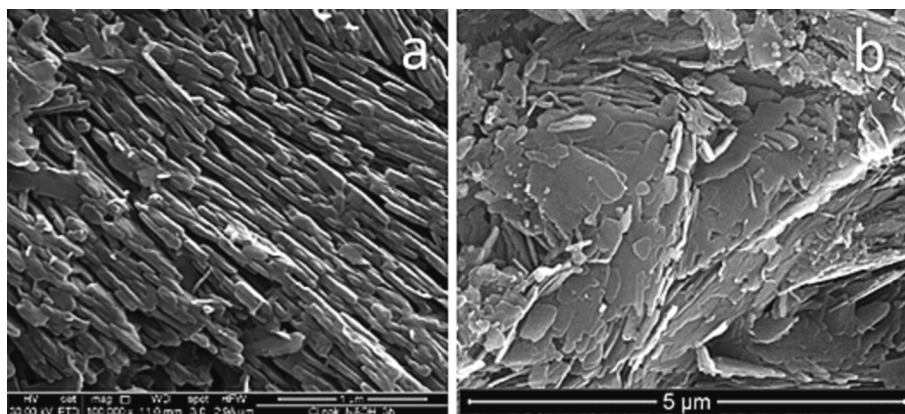


Fig. 5. The mineral named: clinoptilolite is a nature-made nanostructured material, which consists of 40-nm tick single lamellar crystals compactly stacked together (a). These lamellas can be separated by a mechanical treatment based on friction (b).

sinter (coalesce) together without consolidation, as they touch each other with progress of the PVP combustion, thus giving rise to an extended 3D metallic network. In particular, the metallic aerogel is organized in form of cross-linked neck-lace like filaments, as shown in Fig. 6b. Aerogels of silver have been successfully prepared in a very similar way (see Fig. 6c,d). In this case, silver nitrate (AgNO_3) has been reduced by ethylene glycol in presence of PVP and then the obtained silver colloid has been precipitated by acetone addition, dried and thermally annealed in air at $400\text{ }^\circ\text{C}$ in order to completely burn PVP. This high porous metallic structure is named aerogel because it is composed mainly by air and it is therefore an ultralight material. Metallic aerogels are widely permeable to gasses and, owing to the catalytic properties of the noble metals, they can be technologically exploited as catalysts for chemical reactions (e.g., CO conversion to CO_2 , olefin hydrogenation).

Frequently the cleavage of a nature-made nanostructured material leads to technologically useful products. For example, the single-lamellar crystals contained in the clinoptilolite mineral can be separated by a technology based on friction (i.e., tribo-mechanical method) [45]. According to the TEM-micrographs of the achieved samples (see Fig. 7), this mechanical process generates both single-lamellar crystals and small lamellar aggregates (i.e., nanoplatelets). Owing the regular microporosity, which characterizes the zeolite crystal lattice, such nanoplatelets can have many important industrial applications. For example, it is possible to prepare electrically-conductive pastes and solid electrolytes by impregnation of the clinoptilolite nanopowder with a concentrated aqueous solution of inorganic salts and a polymeric binder (e.g., PVP) has been added in order to increase the material cohesion [46]. Further examples of potential technological applications of zeolite lamellas can be: molecular traps for VOCs obtained by using the powder in a supported form (e.g., printed paper functionalized by clinoptilolite nanoplatelets); materials for air dehumidification, ion release systems for agricultural purpose, materials for water purification, etc. [45–46].

Polyoxometalates (POMs) is a class of compounds that has attracted attention of research groups due to their interesting physical properties and nanoscale size [12–25]. POMs represent a diverse class of inorganic compounds mainly constructed by Mo, W, V and Nb at their higher oxidation states (+4, +5, +6) due to the appropriate charge density and

charge-to-ionic radius ratio which: (i) allows the formation of π -bonds with the O^{2-} ligands; (ii) prohibit infinite polymerization and (iii) allows the adoption of several coordination geometries in their metal-oxo complexes ranging from tetrahedral to pentagonal bipyramid. Such coordination flexibility which is associated to the strong metal-oxo bonding explains their ability to undergo controlled polymerization, which leads to structural diversity. On the other hand, group 5 metals, i. e., Nb and Ta; are more restricted in their possible coordination environments and therefore generate small sized building block libraries and form a more limited number of polyanions while Cr oxoanions can only form dimers. POMs due to their wide range of sizes, composition, redox chemistry, photochemistry and charge distribution found a lot of applications in catalysis, molecular electronics, magnetism, material science, and medicine.

Metal-organic framework (MOFs) are constructed by combining metal-containing units with organic linkers, via coordination bonds to form open crystalline framework with permanent porosity. The variations in coordination modes as well as in the geometry of the metal-containing units and organic linkers led to the synthesis of a plethora of compounds which can be rationally designed on the basis of geometrical grounds. In many cases MOFs have excellent porosity which renders them as promising candidates for a wide range of applications such as gas storage, separations and catalysis. Furthermore, their use in energy related applications such as fuel cells, supercapacitors, and catalytic conversion attract the attention of numerous research groups as well as the chemical industry.

In general, nanomaterials are not ‘laboratory curiosities’ but a new very useful form of matter. Indeed, they have been exploited for manifold applications in different technological areas (e.g., optics, photonics, micro-electronics, medicine, robotics). It could be interesting to understand the reason this novel type of matter result so useful for technology. In the industrial applications, material replacement requires the availability of substitutes with equivalent or superior properties. Since nanomaterials are unique matter forms (i.e., they have not any analogues), consequently they cannot be replaced and result extremely needful solutions. In fact, there are technologies whose progress is made possible just by nanomaterials. Nanomaterials have novel properties or combinations of properties that cannot be found in the already exiting massive natural/artificial substances and therefore the advancement of some technologies is strictly related to their development. How could be explained these unique properties of nanomaterials? In general, materials have a set of properties, indeed the specific technologically-useful physical/chemical characteristic is combined with other features, thus providing a material with unique performance in service. For example, a material to be used for optical lens fabrication, in addition to high visible transparency and refractive index close to the glass (ca. 1.5) also possess good mechanical performance, low toxicity, stability to water and chemical solvents, thermal and photochemical stability, etc. In general each material class is characterized by a set of physical/chemical/mechanical/thermal properties and its adequacy for a certain technological application is related to the full set of properties they have. When a material has to be used for some technological application, all features of this set must meet (more or less appropriately) certain specific requirements. Scaling a solid phase to nanometers causes the simultaneous modification of all different matter properties. For example, polymer-embedded coin metals, like gold, silver and copper, on a nanoscopic scale are at same time characterized by light-stable colours (surface plasmon resonance, SPR), perfect transparency (absence of the light-scattering phenomenon), intense visible fluorescence, spin-glass transition, etc. (see Fig. 8). Therefore, the complex combination of properties generated by nanoscaling is unique and cannot be found in any other massive solid systems.

4. The nano-technologies

Nanotechnology is that area of technical knowledge which deals

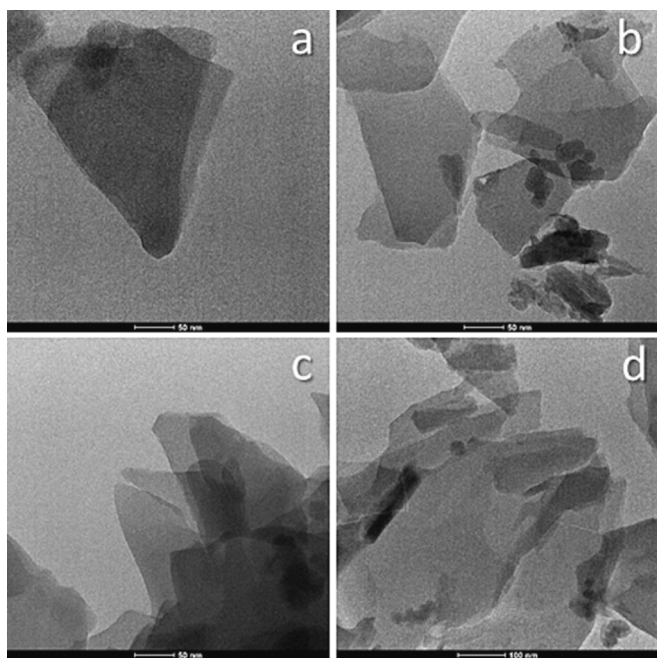


Fig. 7. TEM-micrographs of clinoptilolite lamellar crystals as obtained by the abrasion drill technology.

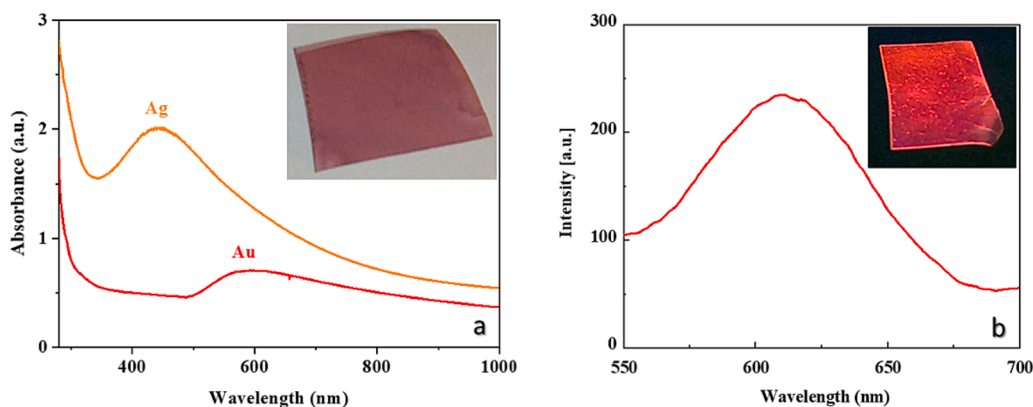


Fig. 8. Surface plasmon resonance of Au and Ag nanoparticles embedded in polystyrene (a) and emission spectrum of Au clusters embedded in polystyrene (b). Both insets evidence the absence of the light-scattering phenomenon. As visible, transparency, fluorescence and colour simultaneously appear in these nanomaterials.

with the development of different practical approaches useful for preparing nanomaterials, like for example the procedures to obtain graphene by means of graphite intercalation/exfoliation or by a chemical oxidation–reduction cycle, or also the pioneering method for the preparation of complex mixtures of carbonaceous materials, including fullerenes, carbon nanotubes, carbon nano-diamonds, etc. based on the use of the electric arc-discharge technique [7,47]. Fig. 9a shows a polymeric film (ethylene vinyl acetate, EVA) coated by a thin layer of graphene. This nanostructured material has been prepared by a micro-mechanical method which is based on the spreading an ultra-fine powder of graphite nanoplatelets (i.e., quasi-graphene) on the flat surface of the polymeric film [48]. The chemical synthesis routes, capable to generate nanostructures like ceramic, metal and semiconductor colloids, metal clusters, semiconductor quantum-dots, etc., also belong to the nanotechnology field. Indeed, alcoholic and hydrazine (or phenylhydrazine) reduction of metal cations, polyol process (see Fig. 9, b-d), metal-carbonyl decomposition by ultrasounds, thermolysis and photolysis of organic-salts (e.g., AuCl, acetyl acetonates, metal thiolates) or

organometallic compounds, and many other techniques named of ‘*Chimie douce*’ have been largely used to produce coin-metal and noble-metal nanoparticles and atomic clusters (mainly: Au, Ag, Pt, and Cu) [49–53]. Chemical synthesis includes also the preparation of: self-assembled 2D nanoparticle monolayers and 3D super-lattices (by using highly monodispersed nanoparticles), cluster compounds (e.g., noble metal nanoparticle derivatized by thiols, $\text{Me}(\text{SR})_n$) [49,50], core/shell metal nanoparticles (e.g., Au@Co, Ag@Ni), composite nanoparticles, etc.

All approaches available for the artificial nanostructure production (both synthesis and extraction technique) have been conventionally categorized as: top-down and bottom-up techniques. The top-down methods consist in the heavy comminution of the bulky crystalline solid, which is achieved for example by laser ablation of metallic targets in liquids, ball-milling in presence of surface passivating agents, etc. Differently, bottom-up techniques consist in the progressive assembly of single atoms or molecules (e.g., $n\text{Me} \rightarrow \text{Me}_n$). The last method allows to achieve nanostructures with very limited nuclearity (i.e., number of atoms or molecules per particle), typically inferior to 1,000, which corresponds to sizes lower than 100 nm; while comminution typically allows to achieve only micronic or slightly sub-micronic particles (i.e., 200–800 nm).

Nanostructures are mostly of artificial origin, that is, they are produced by chemical synthesis or physical methods, however there are also ‘nature-made’ nanostructures that can be extracted from different types of natural sources like for example the magnetotactic bacteria that synthesize iron oxide nanoparticles coated by a biological material named magnetosome [54]; these bacteria use the magnetosomes like a sort of compass to move in the direction of the earth magnetic field. A further example is represented by the graphite that can be used as a source of graphene simply by cleavage of the crystal. The micro-mechanical technique is a very simple and effective technique to obtain polymer-supported graphene from the graphite crystal [55]). Since a number of nanostructured materials are available in nature, a further possibility to achieve nanostructures is by extracting them from natural substances with a tinny featured texture. Such an approach is extremely important for sustainability reasons and recently it has been widely developed. Indeed, chemical reactions are quite harmful for the environment and they must be limited as much as possible in order to reduce world pollution. All these process are of the top-down type. Graphene is probably the most technologically important nanostructure because of its variety of useful physical and chemical properties (electrical conductivity, optical transparency, etc.). Graphene has been prepared for the first time just by the ‘scotch tape’ method, which allows to extract this nanostructure from a widely spread natural substance: the graphite, whose crystalline lattice is made of many graphene sheets compactly stacked together. However, graphite is only one of the many examples of

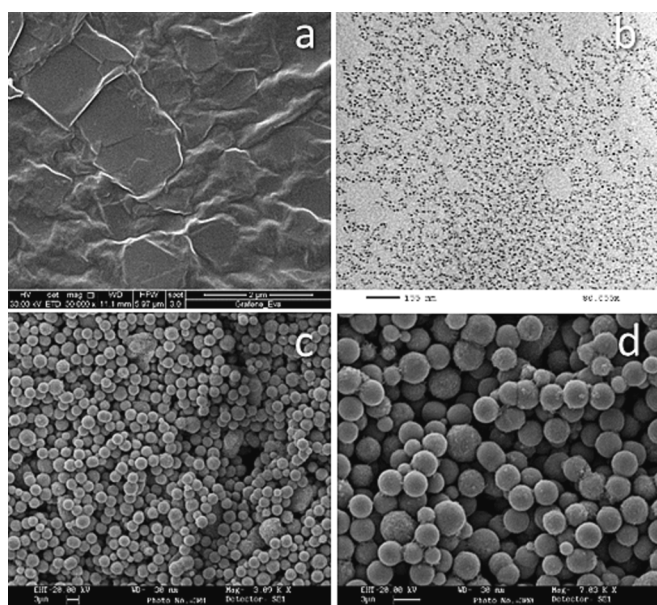


Fig. 9. SEM-micrograph of a graphene layer spread on a polymeric substrate (ethylene vinyl acetate, EVA) (a), TEM-micrograph of iron-polystyrene nanocomposite produced by ex-situ synthesis (i.e., iron nanoparticles were obtained by Fe(II) salt disproportionation and then embedded in polystyrene) (b), and SEM-micrographs at different magnifications of cobalt nanoparticles obtained by the polyol process (c,d).

nanostructured materials available in nature. Further examples are represented by natural zeolites that frequently consists of very compact agglomerates of globular nanostructures or nano-rods or nanoplatelets, etc.

However, nanotechnology refers not only to the fabrication/synthesis of nanomaterials, but also to the nano-manipulation, separation, purification, etc. of these nano-sized solids, like for example the exact positioning of nano-objects on a specific substrate. Magnetic separation, optical tweezers, manipulation with the scanning tunnel microscopy (STM) or atomic force microscopy (AFM), ultracentrifugation, etc. are only some examples of the many advanced nano-manipulation techniques that are available nowadays.

5. The nano-world terminology

All types of concepts and ideas can be more or less successfully communicated. How to correctly communicate an idea? Communication is associated with the concept of precision: a precise communication is capable to transfer unaltered the idea. Various degrees of precision are possible in the transferring and it is convenient that precision is maximized in all cases, especially in the scientific context. Modern scientific disciplines like nanoscience, as they are quite elaborated, strongly require a great precision of the language. That is, they need to express concepts in a way that does not raise any doubt, that avoids misunderstandings. Whatever tool would be useful to increase the precision of communication in the modern disciplines, it could be very advantageously adopted. The Latin/Greek language structure, as a complementary approach to the communication, since it is based on the use of prefixes and suffixes, can certainly be successfully adopted to increase the precision of scientific languages and therefore to facilitate the transferring of concepts/ideas [56]. In addition, this tool can also help in transferring the information in a simplest and fastest way. Indeed, Latin/Greek language structure has been integrated in the nanoscience terminology to allow appropriate definitions for nanostructures and nanotechnologies.

In general, there are several tools for facilitating the communication of concepts/ideas: the use of the most appropriate words, the use of clear examples, the creation of significant images and the use of prefixes are only some of the different possibilities. In nanoscience, in addition to Latin/Greek prefixes, the construction of appropriate words has exploited also the use of special characters, like for example: @, μ - (i.e., micro-), n- (i.e., nano-), chemical formulas, etc.

So far, an enormous variety of regularly-shaped nanostructures have been developed. Owing to such a very large number of available nanostructures, a method for their categorization has been progressively developed, mostly inspired by the nanostructure morphology, which is the most relevant nano-world feature. Such categorization has been simply based on the indication of the chemical composition of the nanostructure and its shape. In particular, the name of each class of nanomaterial is obtained by combining the prefix nano- with the name of the particular geometric shape and adding the chemical substance composition (e.g., silver nano-triangles, gold nano-cubes, carbon nanotubes). Polyhedral particles have a regular shape similar to a sphere, however in the case nanoparticles are not regularly shaped, the Greek prefix: 'pseudo-' has been used (e.g., pseudo-spherical silver nanoparticles). Similarly, quasi-graphene (from the Greek prefix quasi- that means: 'almost') is used to indicate a very thin stacking of graphene sheets (only a few sheets). A further help in the nanostructure classification comes from the use of symbols like @, which means 'at' and has been used for indicating multi-layered systems like the composite core/shell particles of metal, semiconductor and ceramics. For example, Au@Ag nanoparticles corresponds to: silver particles coated by a gold layer (gold on silver), while the term: Au/Ag nanoparticles is used to indicate alloyed-bimetallic particles. As visible, Latin/Greek prefixes have been conveniently used to increase the 'precision' of all scientific terms used in nanoscience: indeed, ultra-fine particles or hyper-fine

particles, and super-lattice terms clearly give the idea of an extremely small-sized solid phase and a very extended lattice, respectively. Further examples are referred to the dimensional scale, like in the case of the word 'porous', that can become the root expressing the fundamental idea to be completed by an adequate prefix. Indeed, the following words can be generated: micro-porous (small-sized porosity, like a molecular porosity), meso-porous (medium-sized porosity) and macro-porous (large-sized porosity). Similarly, the following nouns: 'nano-composite', 'micro-composite', and 'composites' indicate different dimensional scales of the filler used in the biphasic solid system. Even multiple prefixes can be combined together to further increase the precision of this scientific language, for example in addition to nano-metric particles (very small particles, less than 100 nm) and micro-metric particles (some-microns particles), there is also the word: 'sub-micro-metric particles' that is an intermediate case, expressed by combining the two prefixes. Other examples often found in nanoscience are: 'co-precipitation' (in this case, particles and a polymer-stabilizer are precipitated together to produce a solid nanocomposite material); 'ex-situ' and 'in-situ' synthesis (referring to the classification of the chemical synthesis techniques of nanoparticles); 'multi-functional' particles, which refer to particles having many useful physical characteristics, that can be exploited for technological applications, etc. Further examples are given in Table I. In particular, the first column of Tab. I reports the most common scientific prefixes used in nanoscience, as adopted in this work. This prefixes have a Latin or Greek derivation as shown in the second column. The prefix meaning is given in the third column and finally an example of the prefix use is provided in the last column.

Finally, this special approach to the building of precise words makes available, for each nanomaterial class, terms with very specific meanings, thus allowing a correct communication in this modern broad field of knowledge. In nanoscience, Latin/Greek prefixes (see Table 1), as a scientific communication tool, have served to implement the scientific communication skills, by expanding the adaptability of the words. In order to build complex words that appropriately fit the meaning we would give them, we can conveniently use those communication structures developed by the ancient civilizations that are based on the prefixes.

6. Final remarks

According to the above analysis, nanomaterials have represented a great revolution in materials science, and still now they constitute the principal focus of the research in this area. Day by day, nanomaterial

Table 1

Glossary of selected prefixes used in nanoscience. Very precise meanings can be obtained by combining scientific terms with these Latin/Greek prefixes. Nanoscience extensively adopts this communication approach.

Scientific prefix	Latin/Greek derivation	Meaning	Example
Nano-	<i>nanus-</i>	very small	Nano-plate
Pseudo-	<i>ψευδο-</i>	similar	Pseudo-spherical shape
Quasi-	<i>quasi-</i>	almost	Quasi-graphene
Meso-	<i>μεσο-</i>	intermediate	Meso-porous
Micro-	<i>μικρός-</i>	small	Micro-porous
Super-	<i>super-</i>	over	Super-lattice
Supra-	<i>supra-</i>	above, over, beyond	Supra-molecular
Ultra-	<i>ultra-</i>	more than	Ultra-fine particles
Hyper-	<i>hyper-</i>	above, over	Hyper-fine particles
Macro-	<i>μακρός-</i>	big	Macro-porous
Co-	<i>cum-</i>	together	Co-precipitation
Sub-	<i>sub-</i>	under	Sub-micronic
Multi-	<i>multus-</i>	much, many	Multi-shaped nanoparticles
In-	<i>in-</i>	in, into	In-situ synthesis
Ex-	<i>ex-</i>	Out of	Ex-situ synthesis

classes are expanding and a growing number of nano-objects are becoming available, the latest nanomaterials examples are single-atom catalysts [57], advanced ceramic QDs [58,59], MXenes [60], etc. How such a success could be explained and what could be predicted about the future of this class of materials? Clearly, the importance of a certain theoretical or experimental scientific finding (e.g., theory, model, equation, chemical process/reaction) is directly proportional to the number of situations to which such scientific result can be applied. In other words, the 'universality' of the result defines its real relevance. This logical concept could be applied to the case of nanoscience. The possibility to multiply indefinitely the properties of whatever type of solid substance (both elemental substances and chemical compounds) by scaling its size to a nanoscopic range and, at the same time, to finely control these characteristics by changing the morphology/topology (i.e., size, shape, aggregation degree and type, etc.), surely constitutes a very general result. Indeed, although with variable success, the approach of nanomaterials can be potentially applied to many different solid systems, that range from elemental substances to chemical compounds of both organic and inorganic nature (i.e., metals, ceramics, semiconductors, etc.) and include low and high molecular weight substances and supramolecular systems of artificial and natural origin. Also the possibility to generate, by size scaling, properties unavailable in the 'massive/bulk world', whatever type of substance is considered, and to allow multiple-combinations of properties, that typically appear separately in traditional systems is a very general and unique characteristic of the nanoworld. Advanced materials are usually multiphase solids (i.e., composite/hybrid materials), and in the fabrication of these complex solids the use of nanophases constitutes an important potentiality for reaching new properties and tuning them. To increase the number of tuneable characteristics allows the optimization of the final material features with possibility of enhancing the performance of the device that can be obtained. Such 'diversification' approach has shown to be valid for many different classes of substances and therefore to be of a very general validity. As a consequence, the universality of nanoscience makes this approach an extremely useful potentiality, that has been rarely found in the classical materials science areas. The persistent interest for the nanotechnology method, with continuous new theoretical developments and experimental findings, can be explained just on the basis of this simple consideration.

7. Conclusions

The most significant features of the advanced nanomaterials presented in this overview can be summarized in the following points:

- Novel physical and chemical properties arise in the solid matter as an effect of the size scaling. Also the way properties combine together is peculiar in nanomaterials; for example, optical transparency in the visible spectral region (i.e., absence of light-scattering) is typically combined with color, fluorescence, magnetism, EMI shielding, radiopacity, etc.
- Such new properties are caused by many different physical phenomena. Typical physical phenomena determining the unique physico-chemical properties of nanostructures are the following: (i) the electron confinement in semiconductor and metallic quantum-dots (QDs) causes highly-tuneable fluorescence and phosphorescence; (ii) high surface free energy causes super-catalytic effects and the possibility of making stoichiometric solid-state reactions by using nanopowders; (iii) high polarizability of solid noble metal phases (both pure metals and alloys) causes visible surface plasmon resonance; (iv) ferromagnetic metals and metallic alloys scaling to single-domain elements causes super-paramagnetism (i.e., ferromagnetism without remanence).
- The nanoscale matter properties are strictly depending on size and shape and they can be finely tuned by controlling size.

- Regular geometry and monodispersed sizes are characteristics of a fundamental importance for a precise control of properties. Nanostructures are principally used to fabricate functional materials. A system made of identical nanostructures (same shape and size) always is required for functional applications. Indeed, owing to the strict dependence of physical properties on morphology (size and shape) and topology (contact-free dispersions, type of aggregates, etc.), there is the necessity for nanostructures to be monodispersed and regularly shaped. Such an aspect is peculiar of the functionalization based on nanostructures.
- The texture of some natural substance (e.g., zeolites) is characterized by tinny (nanoscopic) features that can be conveniently used to produce nanostructures with unique characteristics potentially exploitable for specific technological applications (e.g., the regular microporosity of the mineral clinoptilolite is useful to fabricate molecular traps for VOCs).

CRediT authorship contribution statement

L. Schiavo: Conceptualization, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **A. Cammarano:** Conceptualization, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **G. Carotenuto:** Conceptualization, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **A. Longo:** Conceptualization, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **M. Palomba:** Conceptualization, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **L. Nicolais:** Conceptualization, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Many pleasant memories bind one of the Authors (L.N.) to prof. H. Alper. They had several profitable opportunities of interaction and collaboration. The Author (L.N.) always appreciated his great commitment with both chemical research and research policies and thanks him very much for the fruitful collaborations and sincere friendship.

References

- [1] S.A. Ahire, A.A. Bachhav, T.B. Pawar, B.S. Jagdale, A.V. Patil, P.B. Koli, *Result. Chem.* (2022), 100633, <https://doi.org/10.1016/j.rechem.2022.100633>.
- [2] S. Mobasser, A.A. Firoozi, *J. Civil Eng. Urban.* 6 (4) (2016) 84–93.
- [3] Zsigmondy RA, (1926). Properties of colloids (Nobel lecture).
- [4] S.S. Salem, E.N. Hammad, A.A. Mohamed, W. El-Dougdoug, *Biointerface Res, Appl. Chem.* 13 (1) (2023) 1–30, <https://doi.org/10.33263/BRIAC131.041>.
- [5] S.J.L. Billinge, Z. Fur Krist. - Cryst. Mater. 217 (7–8) (2002) 282–283, <https://doi.org/10.1524/zkri.217.7.282.23674>.
- [6] D.W. Schaefer, C. Suryawanshi, P. Pakdel, J. Ilavsky, P.R. Jemian, *Phys. A: Statistical Mechanics and its Applications* 314 (2002) 686–695. Doi: 10.1016/S0378-4371(02)01190-1.
- [7] A. Eatemadi, H. Daraee, H. Karimkhanloo, M. Kouhi, N. Zarghami, A. Akbarzadeh, M. Abasi, Y. Hanifehpour, S.W. Joo, *Nanoscale Research Letters* 9 (2014) 393, <https://doi.org/10.1186/1556-276X-9-393>.

- [8] S.F.A. Acquah, A.V. Penkova, D.A. Markelov, A.S. Semisalova, B.E. Leonhardt, J.M. Magi, *ECS J Solid State Sci. Technol.* 6(6) (2017) Doi.M3155-M3162. 10.1149/2.0271706jss.
- [9] A.D. Ghuge, A.R. Shirode, V.J. Kadam, *Curr. Drug Targets* 18 (6) (2017) 724–733, <https://doi.org/10.2174/138945011766616079023425>.
- [10] N. Kumar, R. Salehiyan, V. Chauke, O.J. Botlhoko, K. Setshedi, M. Scriba, M. Masukume, S.S. Ray, *FlatChem* 27 (2021), 100224, <https://doi.org/10.1016/j.flatc.2021.100224>.
- [11] F. Pelayo García de Arquer, D.V. Talapin, V.I. Klimov, Y. Arakawa, M. Bayer, E. H. Sargent, *Sci* 373 (2021) eaaz8541, <https://doi.org/10.1126/science.aaz8541>.
- [12] M. Mirzaei, H. Eshtiagh-Hosseini, M. Arefian, F. Akbarnia, F. Miri, S. Edalatkar-Moghadam, M. Shamsipur, *J. Iran. Chem. Soc.* 12 (2015) 1191–1198, <https://doi.org/10.1007/s13738-014-0581-9>.
- [13] M. Arefian, M. Mirzaei, et al., *Dalton Trans.* 46 (21) (2017) 6812–6829, <https://doi.org/10.1039/C7DT00894E>.
- [14] S. Derakhshanrad, M. Mirzaei, C. Streb, A. Amiri, C. Ritchie, *C. Inorg. Chem* 60 (3) (2021) 1472–1479, <https://doi.org/10.1021/acs.inorgchem.0c02769>.
- [15] M. Bazargan, M. Mirzaei, A. Amiri, J.T. Mague, Opioid drug detection in hair samples using polyoxometalate-based frameworks, *Inorg. Chem.* 62 (1) (2022) 56–65, <https://doi.org/10.1021/acs.inorgchem.2c02658>.
- [16] M. Mirzaei, H. Eshtiagh-Hosseini, M. Alipour, A. Frontera, *A. Coord. Chem. Rev.* 275 (2014) 1–18, <https://doi.org/10.1016/j.ccr.2014.03.012>.
- [17] Z. Khoshkhan, M. Mirzaei, H. Eshtiagh-Hosseini, M. Izadyar, J.T. Mague, M. Korabik, *Polyhedron* 194 (2021), 114903, <https://doi.org/10.1016/j.poly.2020.114903>.
- [18] M. Mirzaei, et al., *Dalton Trans.* 43 (4) (2014) 1906–1916.
- [19] M. Samaniyan, M. Mirzaei, R.M. Gomila, H. Eshtiagh-Hosseini, N. Lotfian, J. T. Mague, A. Frontera, *Dalton Trans.* 50 (5) (2021) 1895–1900.
- [20] M.B. Zarch, M. Mirzaei, M. Bazargan, S.K. Gupta, F. Meyer, J.T. Mague, *Dalton Trans.* 50 (42) (2021) 15047–15056, <https://doi.org/10.1039/D1DT01708J>.
- [21] A. Najafi, M. Mirzaei, J.T. Mague, *CrstEngComm* 18 (35) (2016) 6724–6737, <https://doi.org/10.1039/C6CE01183G>.
- [22] M. Mirzaei, H. Masoud, H. Eshtiagh-Hosseini, A. Alipour, J.T. Bauzá, M. Mague, A. F. Korabik, *Dalton Trans.* 44 (19) (2015) 8824–8832, <https://doi.org/10.1039/C4DT03950E>.
- [23] M.A. Fashapoyeh, M. Mirzaei, H. Eshtiagh-Hosseini, A. Rajagopal, M. Lechner, R. Liu, C. Streb, *Chem. Commun.* 54 (74) (2018) 10427–10430, <https://doi.org/10.1039/C8CC06334F>.
- [24] M. Bazargan, M. Mirzaei, A. Franconetti, A. Frontera, *Dalton Trans.* 48 (17) (2019) 5476–5490, <https://doi.org/10.1039/C9DT00542K>.
- [25] H.N. Miras, L. Vilà-Nadal, L. Cronin, *Chem. Soc. Rev.* 43 (16) (2014) 5679–5699.
- [26] C.L. Nehl, H. Liao, J.H. Hafner, *Nano Lett.* 6 (4) (2006) 683–688, <https://doi.org/10.1021/nl052409y>.
- [27] V. Singh, P. Yadav, V. Mishra, Recent advances on classification, properties, synthesis, and characterization of nanomaterials, *Green Synthesis of Nanomaterials for Bioenergy Applications*, Chapter 3 Edited by Neha Srivastava, Published by John Wiley & Sons Ltd. (2020), 83–97.
- [28] N. Faisal, K. Kumar, *Biointerface Res. Appl. Chem.* 7(6) (2017) 2286–2294. DOI10.1016/j.jmsec.2015.11.023.
- [29] O.M. Folarin, E.R. Sadiku, A. Maity, *Int. J. Phys. Sci.* 6 (21) (2011) 4869–4882, <https://doi.org/10.5772/intechopen.79016>.
- [30] R.C. Zhang, D. Sun, R. Zhang, W.F. Lin, M. Marcias-Montero, J. Patel, S. Askari, C. McDonald, D. Mariotti, P. Maguire, *Scient. Rep.* 7 (2017) 46682, <https://doi.org/10.1038/srep46682>.
- [31] Q. Chen, *Nano Lett.* 22 (2022) 3–5, <https://doi.org/10.1021/acs.nanolett.1c03400>.
- [32] E. Matijevic, *Fine Particle: science and technology*, *MRS Bull.* 14 (1989) 18–20.
- [33] H. Remita, J. Khatouri, M. Tréguer, J. Amblard, J. Belloni, *Z. Phys. D: Atoms, Molecules Clusters* 40 (1997) 127–130, <https://doi.org/10.1007/s004600050175>.
- [34] V. Harish, D. Tewari, M. Gaur, A.B. Yadav, S. Swaroop, M. Bechelany, A. Barhoum, *Nanomater.* 12 (2022) 457, <https://doi.org/10.3390/nano12030457>.
- [35] E.L. Ayuk, U. Mariagoretti, A. Samuel, *Chem. Res. J.* 2 (5) (2017) 97–123, <https://doi.org/10.3390/nano12030457>.
- [36] L. Keshavarz, M. Reza Ghaani, J.M. Don MacElroy, N.J. English, *Chem. Eng. J.* 412 (2021), 128604, <https://doi.org/10.1016/j.cej.2021.128604>.
- [37] J. Feng, B.L. Su, H. Xia, S. Zhao, C. Gao, L. Wang, O. Ogbeide, J. Feng, T. Hasan, *Chem. Soc. Rev.* (2021), <https://doi.org/10.1039/C9CS00757A>.
- [38] J.H. Lee, S.J. Park, *Carbon* 163 (2020) 1–18, <https://doi.org/10.1016/j.carbon.2020.02.073>.
- [39] S. Kashyap, S. Kabra, B. Kandasubramanian, *J. Mater. Sci.* 55 (10) (2020) 4127–4156, <https://doi.org/10.1007/s10853-019-04325-7>.
- [40] H.Y. Zhao, M.Y. Yu, J. Liu, X. Li, P. Min, Z.Z. Yu, *Nano-Micro Lett.* 14 (2022) 129, <https://doi.org/10.1007/s40820-022-00878-6>.
- [41] X. Jiang, R. Du, R. Hübner, Y. Hu, A. Eychmüller, *Matter* 4 (2021) 54–94, <https://doi.org/10.1016/j.matt.2020.10.001>.
- [42] X. Zhang, C. Wang, K. Chen, A.H. Clark, R. Hübner, J. Zhan, L. Zhang, A. Eychmüller, B. Cai, *Adv. Mater.* 35 (2023) 2211512, <https://doi.org/10.1002/adma.202211512>.
- [43] L. Schiavo, S. De Nicola, G. Carotenuto, *Nanoscale Res. Lett.* (2018) 13, <https://doi.org/10.1186/s11671-017-2422-0>.
- [44] L. Schiavo, L. Aversa, R. Tatti, R. Verucchi, G. Carotenuto, *J. Anal. Methods Chem.* No. 9073594 (2016), <https://doi.org/10.1155/2016/9073594>.
- [45] L. Schiavo, V. Boccia, L. Aversa, R. Verucchi, G. Carotenuto, T. Valente, *Mater. Proc.* 14 (1) (2023) 11, <https://doi.org/10.3390/IOC2023-14474>.
- [46] X. Chi, M. Li, J. Di, P. Bai, L. Song, X. Wang, F. Li, S. Liang, J. Xu, J. Yu, *Nature* 592 (7855) (2021) 551–557, <https://doi.org/10.1038/s41586-021-03410-9>.
- [47] D.V. Schur, S.Y. Zaginaichenko, *Carbon nanostructured materials – I, Nanoscience and Nanotechnologies Encyclopedia of Life Support Systems (EOLSS)*.
- [48] G. Carotenuto, S. De Nicola, G. Ausanio, D. Massarotti, L. Nicolais, G.P. Pepe, *Nanoscale Res. Lett.* 9 (2014) 475, <https://doi.org/10.1186/1556-276X-9-475>.
- [49] L. Nicolais, G. Carotenuto (Eds.), *Metal-Polymer Nanocomposites*, John Wiley & Sons, Hoboken, NJ, USA, 2005.
- [50] L. Nicolais, G. Carotenuto, . G. (Eds.), *Nanocomposites: in Situ Synthesis of Polymer-Embedded Nanostructures*, John Wiley & Sons, Hoboken, NJ, USA, 2013.
- [51] L. Nicolais, G. Carotenuto, *Functional and multifunctional nanostructured materials, in Multifunctionality of Polymer Composites - Challenges and New Solutions*, Edited by Klaus Friedrich Ulf Breuer. Elsevier (2015), 842–857.
- [52] G. Carotenuto, L. Nicolais, *Graphene-polymer composites*, *Wiley Encyclopedia of Composites*, II edition, Edited by Luigi Nicolais and Assunta Borzacchiello, John Wiley & Sons, Hoboken, NJ, USA, 2012.
- [53] G. Carotenuto, C. Giannini, D. Siliquì, L. Nicolais, *Preparation of polymer-embedded metal and metal sulfide clusters*, *Wiley Encyclopedia of Composites* (2011) 1–4.
- [54] L. Chen, D.A. Bazylinski, B.H. Lower, *Bacteria that synthesize nano-sized compasses to navigate using earth's geomagnetic field*, *Nature Education Knowledge* 3 (10) (2010) 30.
- [55] J. Wei, T. Vo, F. Inam, *RSC Adv.* 5 (2015) 73510–73524, <https://doi.org/10.1039/C5RA13897C>.
- [56] P. Loyson, *J. Chem. Educ.* 87 (12) (2010) 1303–1307, <https://doi.org/10.1021/ed1000894>.
- [57] K. Dang, H. Dong, L. Wang, M. Jiang, S. Jiang, W. Sun, Y. Tian, *Adv. Mater.* 34 (27) (2022) 2200302, <https://doi.org/10.1002/adma.202200302>.
- [58] W. Xun, Y. Li, *Chem. Commun.* (2007) 2901–2910, <https://doi.org/10.1039/B700183E>.
- [59] J. Aldana, N. Lavelle, Y. Wang, X. Peng, *J. Am. Chem. Soc.* 127 (8) (2005) 2496–2504, <https://doi.org/10.1021/ja047000>.
- [60] Y. Cui, U. Banin, M.T. Björk, A.P. Alivisatos, *Nano Lett.* 5 (7) (2005) 1519–1523, <https://doi.org/10.1021/nl051064g>.